

Atomistic Molecular Dynamics Simulation Study of a Hybrid Poly (ethylene oxide) / Silica Nanoparticle System

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ABSTRACT SUMMARY:

In this work results from detailed atomistic molecular dynamics simulations of bulk poly(ethylene oxide) (PEO) and a hybrid system of poly(ethylene oxide) with a silica (SiO₂) nanoparticle are presented. For both systems polymer density profiles, as well as structural and dynamical properties of polymer chains, are calculated. For the hybrid system the various properties were also calculated as a function of the distance from the nanoparticle and compared with the corresponding bulk values.

INTRODUCTION:

Polymers are often filled with inorganic compounds in order to improve their properties. The goal of the present work is to study organic/inorganic nanostructured materials at the molecular level and predict their structure-properties relations, through detailed atomistic simulations. Here we focus on polymer/silica nanoparticle hybrid systems. Such nanocomposites constitute a relatively new class of materials that has attracted growing scientific and technological interest.

Poly (ethylene oxide), PEO, is a non-ionic, water – soluble, semi crystal polymer with many applications; for example its hydrophilicity, biocompatibility, and versatility make it attractive for biotechnological applications. In addition, PEO is a favorable candidate for the development of solid polymer electrolytes with high ionic conductivity because of its ability to dissolve large amounts of salt and its structure, which supports ion transport. Despite its pronounced crystalline character that inhibits the cation mobility.

In this work we perform detailed atomistic Molecular Dynamics simulations on a hybrid system of PEO with a Silica nanoparticle, in order to study and understand the structural and dynamical properties of the hybrid system. In more detail, we directly calculate the density profile, chain conformations, segmental and terminal dynamics of PEO chains as a function of distance from the silica nanoparticle.[4-5] In a further step we will compare the simulation results to experimental data.

SIMULATION METHOD:

Atomistic NPT Molecular Dynamics (MD) simulations were performed for bulk PEO and PEO/Silica nanoparticle systems. The pressure was kept constant at 1 atm using the Parrinello-Rahman barostat. The Nose-Hoover thermostat was used to maintain the temperature value at 318K. Moreover a series of different temperatures between (270-330)K were examined. A united atom model was used for the PEO and chains of 10 monomers were simulated. The modified Tra-PPE force field¹ was used for the description of the non-bonded interactions, whereas electrostatic interactions were calculated via the particle-mesh Ewald method (PME). The cutoff distance was 0.9nm for both van der Waals and electrostatic interactions. Bond lengths were kept constant using SHAKE algorithm. For the interaction between polymer atoms and silica nanoparticle the Lorentz-Berthelot combination rules were used with: $\epsilon_{\text{SiSi}}/k_B=301.936\text{K}$, $\epsilon_{\text{OO}}/k_B=76.59\text{K}$, $\epsilon_{\text{HH}}/k_B = 11.065\text{K}$ and $\sigma_{\text{SiSi}}=3.92\text{\AA}$, $\sigma_{\text{OO}}=3.154\text{\AA}$, $\sigma_{\text{HH}} = 2.352\text{\AA}$. We simulated a bulk system of 48 and 144 chains and two hybrid PEO/SiO₂ systems. In the current study one nanoparticle (NP) of radius equal to 2nm is contained in the polymer matrix. Details about all model systems are given In Table 1.

Table 1: *Systems' Details*

Small system			
Radius of NP	Number of atoms in the system	Number of atoms in NP	Number of chains
2.0 nm	14589	3069	384
Large system			
Radius of NP	Number of atoms in the system	Number of atoms in NP	Number of chain
2.0 nm	37629	3069	1152

RESULTS AND DISCUSSION:

Bulk system:

The density of a bulk PEO system as a function of temperature is presented in Figure 1. As expected a monotonic decrease of density with temperature increasing is observed.

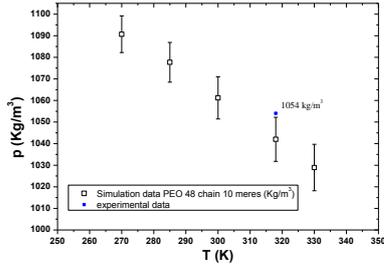


Fig. 1: Density of PEO as a function of temperature.

An experimental value at 318K is also included in the figure (solid symbol). We observe that our model underestimates the bulk density by almost 1%. Error bars are also included in the figure and are of the order of 1% of the actual value.

In the following results concerning segmental and terminal dynamics of bulk PEO chains are presented. The time autocorrelation functions for a vector defined along the backbone of the polymer chain connecting two non-consecutive united atoms (\mathbf{v}_{1-3}) and the end-to-end vector (\mathbf{R}_{ee}) are depicted in Figure 2 for a bulk PEO system at $T=318$ K.

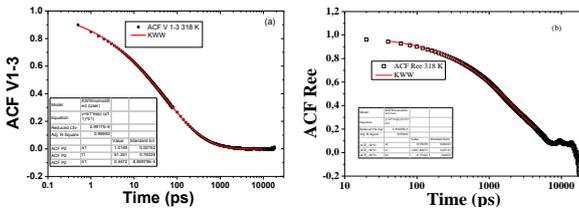


Fig. 2: Time autocorrelation functions of (a) \mathbf{v}_{1-3} vector (segmental dynamics) and (b) \mathbf{R}_{ee} vector (terminal dynamics) as a function of time for a bulk PEO system at $T=318$ K.

Both curves are fitted with a Kohlrausch-Williams-Watts (KWW) function of the form (1):

$$P_2(t) = A \exp \left[- \left(\frac{t}{t_{KWW}} \right)^\beta \right] \quad (1)$$

from which we extract information for the segmental and the molecular (terminal) relaxation times respectively. Relaxation times for various temperatures are presented in Figure 3a while the corresponding β -exponents are depicted in Figure 3b. As expected the relaxation time decreases with the increase of temperature because of the higher mobility of the polymer chains. Moreover segmental relaxation time is faster than the terminal one, whereas the distribution of segmental relaxation time is broader (β -exponent is smaller) than the distribution of the terminal ones. Additionally, the values of β -exponent for both vectors do not depend on the temperature, for the range of temperatures studied here.

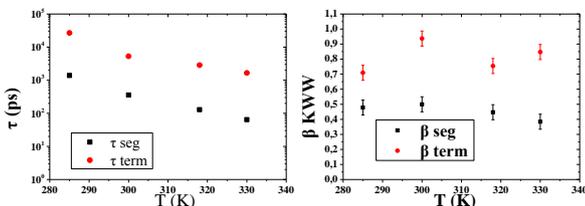


Fig. 3: Relaxation times as a function of temperature (segmental and terminal dynamics) (left). Beta exponents as a function of temperature (segmental and terminal dynamics) (right).

Hybrid system (PEO/Silica NP):

In figure 4 a snapshot of a Silica NP in a polymer matrix containing 1152 PEO chains is presented.

Next, in Figure 5 we present the density profiles of PEO as a function of the distance from the center of mass of the silica NP for the two systems. Density profiles are calculated for the center of mass of the monomer. We observe that the large system attains the bulk density at long distances, whereas this is not the case for the small one. Bulk density is represented with the horizontal line.

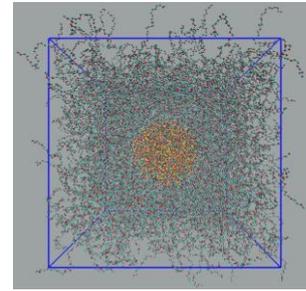


Fig. 4: Snapshot of Silica NP in PEO matrix

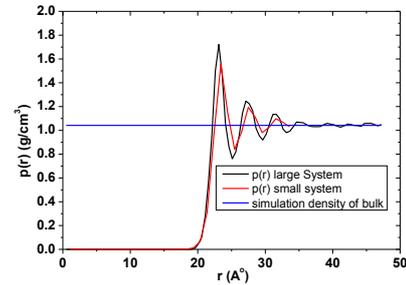


Fig. 5: Monomer density profile as a function of the distance from the center of mass of silica NP.

CONCLUSIONS:

In this work we studied bulk PEO and hybrid PEO/Silica systems through atomistic molecular dynamics simulations. Our model predicts well the density of bulk PEO (1-2%, lower than the experimental values), as well as its thermal expansion coefficient (data not shown here).

Our preliminary results of the PEO density profile for the hybrid PEO/Silica system indicate the proper size of system in order to reach the bulk density away from the silica nanoparticle.

Our current work concerns the analysis of the segmental and terminal dynamics of PEO chains in the hybrid system, following previous works.^{4,5} Furthermore the examination of the effect of the size of the NP, as well as of different PEO molecular weights is in progress. Finally simulation results will be compared against available experimental data.

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